

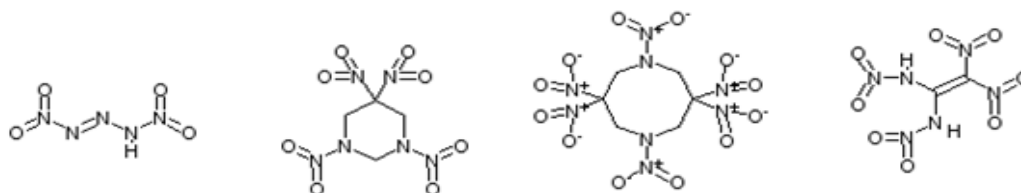


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Environmental Screening Assessment of Perchlorate Replacements

Jay L. Clausen, Stephen Clough,
Michael Gray, and Patrick Gwinn

August 2007



COVER: Chemical structures for ammonium di(nitramido)amine (ADNA); 1,3,5,5-tetranitrohexahydropyrimidine (DNNC), 1,3,3,5,7,7-hexanitro-1,5-diazacyclopentane (HCO), and diammonium di(nitramido)dinitroethylene (ADNDNE).

Environmental Screening Assessment of Perchlorate Replacements

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Final report

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Abstract: A screening level assessment of the fate, transport, and toxicity of four potential replacements for perchlorate was performed. Resulting data will allow for evaluation and minimization of the potential environmental liability associated with the use of energetic compounds as propellants. This report details methods used and assessment findings. Inorganic oxidizer ammonium di(nitramido)amine (ADNA); cyclic nitramine/gem-dinitro compound 1,3,5,5-tetranitrohexahydropyrimidine (DNNC); 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HCO); and diammonium di(nitramido)dinitroethylene (ADNDNE) were evaluated. Their respective analogue compounds also were evaluated: ammonium dinitramide (ADN); hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); and 1,1-diamino-2,2-dinitroethene (FOX-7). Evaluations of ammonium perchlorate (AP) provide a point of comparison. From an environmental fate and transport perspective, it appears ADNA, ADNDNE, DNNC, and HCO may have some characteristics similar to AP. However, it is possible HCO and DNNC are much less soluble in water than AP, thereby reducing the likelihood of environmental transport. It also is anticipated that ADNA, ADNDNE, DNNC, and HCO will readily photodegrade. However, rates of degradation in subsurface soil, groundwater, deep surface water, and sediment appear highly variable and may be dependent on covariables not evaluated for this assessment. Because of uncertainty with the model predicted results, recommendations for additional analysis, which could yield compound-specific data and reduce uncertainty, are provided.

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NOMENCLATURE

ADN	Ammonium dinitramide
ADNA	Ammonium di(nitramido)amine
ADNDNE	Diammonium di(nitramido)dinitroethylene
AP	Ammonium perchlorate
CAS	Chemical Abstract Services
DNNC	1,3,5,5-tetranitrohexahydropyrimidine
EPI	Estimation Program Interface
FOX-7	1,1-diamino-2,2-dinitroethene
HCO	1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane
HLC	Henry's Law Constant
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
K _{oc}	Organic carbon soil sorption coefficient
K _{ow}	Octanol water partitioning coefficient
LOEC	Lowest observed effect concentration
NSWC	Naval Surface Warfare Center
QSAR	Quantitative structure activity analysis
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
SERDP	Strategic Environmental Research and Development Program
SMILES	Simplified Molecular Input Line Entry System
USEPA	United States Environmental Protection Agency

EXECUTIVE SUMMARY

A screening level assessment of the fate, transport, and toxicity of four potential replacements for perchlorate was performed to support the Strategic Environmental Research and Development Program (SERDP) project PP-1403 “Synthesis, Evaluation, and Formulation Studies on New Oxidizers as Alternatives to Ammonium Perchlorate in DoD Missile Propulsion Applications.” Data derived from this project will allow for evaluation and minimization of the potential environmental liability associated with the use of energetic compounds as propellants. This report details the methods used and the findings of our assessment.

Compounds evaluated in this screening level assessment include the inorganic oxidizer ammonium di(nitramido)amine (ADNA); the cyclic nitramine/gem-dinitro compound 1,3,5,5-tetranitrohexahydropyrimidine (DNNC); 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HCO); and diammonium di(nitramido)dinitroethylene (ADNDNE). In addition to these, the following analogue compounds were evaluated: ammonium dinitramide (ADN) as an analogue for ADNA; hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) as an analogue for DNNC; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as an analogue for HCO; and 1,1-diamino-2,2-dinitroethene (FOX-7) as an analogue for ADNDNE. Evaluations of ammonium perchlorate (AP) provide a point of comparison.

Empirically derived literature values and Quantitative Structure Activity Analysis (QSAR) modeling data provided an assessment of the environmental fate of the chemicals of interest. The QSAR analysis was conducted using the US Environmental Protection Agency’s computer program, Estimation Program Interface (EPI) Suite. Evaluations of data from literature and EPI Suite provided an estimate of each chemical’s likely behavior in the environment and an assessment of the uncertainty of EPI Suite model output.

From the screening level analysis, it appears ADNA, ADNDNE, DNNC, and HCO may have some characteristics similar to AP from an environmental fate and transport perspective. However, it is possible HCO and DNNC are much less soluble in water than AP, thereby reducing the likelihood of environmental transport. It also is anticipated that ADNA,

ADNDNE, DNNC, and HCO will readily photodegrade. However, rates of degradation in subsurface soil, groundwater, deep surface water, and sediment appear highly variable and may be dependent on covariables not evaluated for this assessment. Because of uncertainty with the model predicted results, recommendations for additional analysis , which could yield compound-specific data and reduce uncertainty, are provided.

PREFACE

This report was prepared by Jay L. Clausen, Biogeochemical Sciences Branch (BSB), US Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire; Stephen Clough, Haley and Aldrich, Inc., Manchester, New Hampshire; and by Michael Gray and Patrick Gwinn, AMEC Earth and Environmental, Inc., Portland, Maine.

This work was funded by the US Navy, Naval Surface Warfare Center (NSWC) Indian Head, in support of Strategic Environmental Research and Development Program (SERDP) Project PP-1403, "Synthesis, Evaluation, and Formulation Studies on New Oxidizers as Alternatives to Ammonium Perchlorate in DoD Missile Propulsion Applications."

Dr. Charles M. Reynolds and Dr. David B. Ringelberg, BSB, ERDC-CRREL, provided technical reviews.

This report was prepared under the general supervision of Terrence M. Sobecki, Branch Chief, BSB, CRREL; Dr. Justin B. Berman, Chief, Research and Engineering Division, CRREL; and Dr. Robert E. Davis, Director, CRREL.

At the time this work was performed, Colonel Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

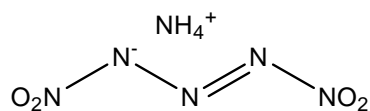
1 INTRODUCTION

The military is continuously researching and developing improved replacement propellants and explosive materials for use in munitions. Chemical propellants and explosives can undergo research and development for years and are tested for a variety of chemical and physical properties related to their suitability for use in munitions. Moreover, at any one time there can be numerous compounds in various stages of development. Significant personnel as well as financial resources are dedicated to the development of these compounds. Identification of less suitable compounds or ones having additional environmental liability early in the development process aids in focusing resources on those compounds with maximum application potential and minimal environmental liability.

Historically, the evaluation of success or failure of these compounds has focused on their performance as energetic materials, whereas little attention has been paid to the potential environmental liability during the life-cycle developmental process. More recently, environmental mobility, persistence, and potential toxicity issues related to perchlorate have highlighted the importance of trying to anticipate the environmental risk before beginning large-scale production of a new oxidizer, i.e., assessment of the environmental impact needs to be performed before embarking on an expensive synthesis effort. Recognizing this issue, an assessment of the fate and transport and toxicological properties of new oxidizers proposed to replace perchlorate in rocket propellant formulations was deemed necessary to support the Strategic Environmental Research and Development Program (SERDP) project PP-1403 "Synthesis, Evaluation, and Formulation Studies on New Oxidizers as Alternatives to Ammonium Perchlorate in DoD Missile Propulsion Applications." The work was performed for Dr. Randall Cramer with the Naval Surface Warfare Center (NSWC), which partnered with ATK Thiokol, Inc., on the project. The predictive assessment uses a uniquely defined architecture to evaluate whether the new oxidizers proposed to replace perchlorate are more or less environmentally benign relative to perchlorate.

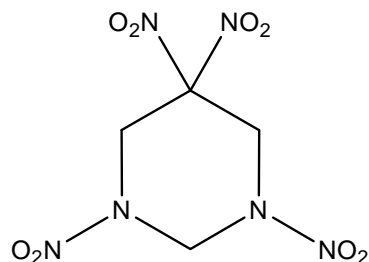
NSWC has identified four energetic chemicals that are being considered for future use. These include the inorganic oxidizer ammonium di (nitra-

mido) amine (ADNA), whose chemical structure is presented in Figure 1; the cyclic nitramine/gem-dinitro compound 1,3,5,5-tetranitrohexahydropyrimidine (DNNC), whose chemical structure is presented in Figure 2; 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HCO), whose chemical structure is presented in Figure 3; and diammonium di(nitramido) dinitroethylene (ADNDNE) whose chemical structure is presented in Figure 4¹.



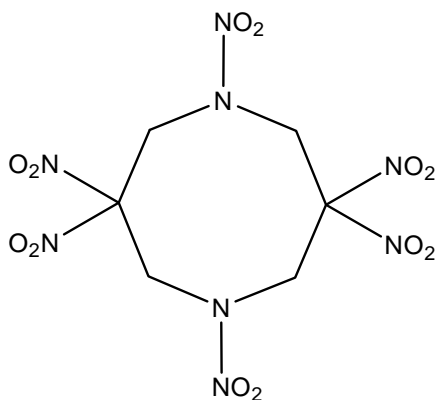
$\rho = 1.76 \text{ g/mL (calc)}$
 $\Delta H_f = +43 \text{ kcal/mole (calc)}$

Figure 1. ADNA



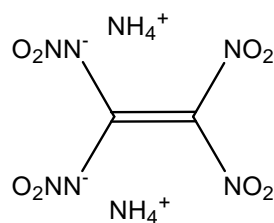
$\rho = 1.82 \text{ g/mL}$
 $\Delta H_f = +11 \text{ kcal/mole}$
 $mp = 151-4 \text{ degrees C}$

Figure 2. DNNC



$\rho = 1.875 \text{ g/mL}$
 $\Delta H_f = -6.52 \text{ kcal/mole}$
 $mp = 250 \text{ degrees C (dec)}$

Figure 3. HCO



$\rho = 1.77 \text{ g/mL (calc)}$
 $\Delta H_f = 4.02 \text{ kcal/mole (calc)}$

Figure 4. ADNDNE

Figures 1–4. Structure of ADNA, DNNC, HCO, and ADNDNE.

¹ The EPI Suite model is unable to evaluate ionic bonds such as those found in ADNA. A surrogate for ADNA was used and can be viewed in Figure 6.

This report describes the methods used to estimate fate, transport, and toxicological information on the four subject compounds in Section 2. Section 4 discusses the findings in terms of the estimated fate, transport, and toxicity with respect to ammonium perchlorate and presents the uncertainties associated with this analysis. Section 5 presents a discussion of the findings and Section 6 provides conclusions and recommendations.

2 OBJECTIVES

Literature, where available, and the Estimation Program Interface (EPI) Suite Quantitative Structure Activity Relationship (QSAR) model were used to determine or predict the fate, transport potential, and toxicological properties of the four oxidizers of interest. Data generated for the four oxidizers were contrasted with the chemical and physical properties of perchlorate for a basis of comparison. Then an assessment was made as to whether the oxidizer of interest is more or less benign than perchlorate. The concern is the release of potentially toxic compounds that subsequently leach into groundwater or surface water during the use of ordnance for testing and training at military bases. Therefore, exposure is primarily determined by the chemicals' propensity to disperse, i.e., to contaminate soil and quickly migrate to surface water or groundwater.

Task 1 consisted of a literature search to obtain any relevant information on fundamental properties that affect fate, transport, and toxicity of the four proposed compounds. If data on the primary oxidizer were not available, a literature search was conducted for surrogate chemicals (i.e., chemicals that have similar chemical structures and that may behave in a way similar to the oxidizer being considered).

Task 2 entailed conducting an initial screening and ranking using QSAR models (e.g., EPIWIN, ECOSAR) that predict the physicochemical properties of a chemical, disposition in various environmental media, and subsequent toxicity should receptor exposure occur. These models work by comparing the structure of the oxidizer in question to large chemical libraries containing thousands of similar compounds that already have known environmental properties. These properties are further regressed against known environmental behavior endpoints, such as persistence, bioaccumulation, and toxicity. The EPI Suite output provides a reasonably accurate assessment of how the chemical might partition to air, water, soil, and sediment if introduced into the general environment.

Some of the predictive output parameters are the octanol–water partition coefficient (K_{ow}), water solubility, Henry's Law Constant, propensity to biodegrade, half-life in air, soil adsorption coefficient, and half-life in sur-

face water. Those chemicals that rank lowest for potential environmental mobility and toxicity were subject to fugacity modeling to estimate equilibrium concentrations in various environmental compartments (assuming a known flux to soil, air, water, sediment, and biota).

Data generated from the literature review and the QSAR modeling were used to rank the new compounds against perchlorate from a fate-and-transport/toxicology prospective. The comparative ranking was limited to data generated as part of the literature review and QSAR modeling. It is important to note this screening-level analysis does not allow for a comparison of all physiochemical and toxicological properties known for perchlorate. For example, studies of subtle chronic health effects of the proposed oxidizers are not available, nor is this information generated as part of the proposed QSAR modeling. In contrast, data on subtle chronic health effects for perchlorate are available. As a result of the incomplete datasets, a comparison of chronic health effects is not possible. Nevertheless, the data generated and used for the comparison are significant in their ability to assess the environmental behavior of the proposed oxidizers with respect to perchlorate.

3 METHODS

The methods used in the assessment include the following:

1. Literature search to develop a database of known physical and chemical characteristics for each of the subject chemicals;
2. Screening evaluation of each chemical using QSARs to estimate physical and chemical data that are not known or found in the literature; and
3. Assessment of the uncertainty in the QSAR analysis by evaluating similar surrogate chemicals with measured and published physical and chemical data.

3.1 Literature Search

DIALOG database and Internet literature searches were conducted to obtain relevant information on fundamental properties affecting the fate, transport, and toxicity of the four proposed compounds and other surrogate compounds. DIALOG is a collection of millions of documents drawn from more sources than any other online searchable database service. Also, data for structurally similar compounds were obtained as part of the literature search. The DIALOG databases searched include

1. INSPEC: The Database for Physics, Electronics and Computing (1969–present);
2. NTIS: National Technical Information System;
3. Ei Compendex: Worldwide coverage of approximately 4,500 journals and selected government reports and books;
4. Science Search: An international, multidisciplinary index to the literature of science, technology, biomedicine, and related disciplines (1991–present);

5. Energy Science Technology (formerly DOE ENERGY): A multi-disciplinary file containing worldwide references to basic and applied scientific and technical research literature (1976–present);
6. Wilson Applied Science & Technology Abstracts: Comprehensive abstracting and indexing of more than 400 core English-language scientific and technical publications;
7. Chapman & Hall Chemical Database (CHCD) (formerly HEILBRON): A chemical properties database representing the complete text of several chemical dictionaries from Chapman and Hall;
8. Chemical Engineering and Biotechnology Abstracts (CEABA): A database corresponding to the printed publications *Chemical Engineering* and *Biotechnology Abstracts*.

In addition to the Dialog search, the Internet was searched for publicly available databases such as Storming Media. Also, relevant sources were searched for information in the published literature on the environmental and toxicological properties of the explosives and propellants in production by the US military. Technical reports and journal articles that were deemed to be relevant to this project were retrieved and reviewed. Data collected as part of the literature search and review effort were used as initial input into the QSAR computer program discussed below. Despite finding a large number of technically relevant materials in the literature search, few empirical data were available for the subject compounds ADNA, DNNC, HCO, and ADNDNE. Appendix A summarizes the data found in the literature on these compounds.

3.2 Estimation Program Interface (EPI) Suite

EPI Suite is a publicly available Windows-based suite of physical/chemical property and environmental fate estimation models developed by the US Environmental Protection Agency (USEPA). Currently, no published validation or sensitivity studies have been conducted; consequently, EPI Suite is scheduled for an EPA Science Advisory Board review sometime in 2007. EPI Suite comprises individual chemical/physical estimating modules, each designed to estimate a specific physical or chemical property of a given structure.

- KOWWIN: Estimates the log K_{ow} of chemicals using an atom/fragment contribution method;
- AOPWIN: Estimates the gas-phase reaction rate between the most prevalent atmospheric oxidant, hydroxyl radicals, and a chemical. Gas-phase ozone radical reaction rates are also estimated for olefins and acetylenes. AOPWIN also informs the user if nitrate radical reaction will be important. Atmospheric half-lives for each chemical are automatically calculated using assumed average hydroxyl radical and ozone concentrations;
- HENRYWIN: Calculates the Henry's Law Constant (air/water partition coefficient) using both the group contribution and the bond contribution methods.
- MPBPWIN: Melting point, boiling point, and vapor pressure of organic chemicals are estimated using a combination of techniques.
- BIOWIN: Estimates aerobic biodegradability of organic chemicals using six different models; two are the original Biodegradation Probability Program (BPP).
- PCKOCWIN: The ability of a chemical to sorb to soil and sediment, its soil adsorption coefficient (K_{oc}), is estimated by this program. The K_{oc} estimations are based on the Sabljic molecular connectivity method with improved correction factors.
- WSKOWWIN: Estimates a K_{ow} using the algorithms in the KOWWIN program and estimates a chemical's water solubility from this value. This method uses correction factors to modify the water solubility estimate based on regression against log K_{ow} .
- HYDROWIN: Acid- and base-catalyzed hydrolysis constants for specific organic classes are estimated by HYDROWIN. A chemical's hydrolytic half-life under typical environmental conditions also is determined. Neutral hydrolysis rates currently are not estimated.

- BCFWIN: Calculates the BioConcentration Factor and its logarithm from the log K_{ow} . The methodology is analogous to that for WSKOWWIN. Both are based on log K_{ow} and correction factors.
- WVOLWIN: Estimates the rate of volatilization of a chemical from rivers and lakes and calculates the half-life for these two processes from their rates. The model makes certain default assumptions such as water body depth, wind velocity, etc.
- STPWIN: Using several outputs from EPIWIN, this program predicts the removal of a chemical in a Sewage Treatment Plant; values are given for the total removal and three contributing processes (biodegradation, sorption to sludge, and stripping to air) for a standard system and set of operating conditions.
- LEV3EPI: This level III fugacity model predicts partitioning of chemicals between air, soil, sediment, and water under steady state conditions for a default model “environment”; the user can change various defaults.

EPI Suite runs from a single input, i.e., the chemical structure in Simplified Molecular Input Line Entry System (SMILES) notation. The notation can be created and pasted into the input screen or obtained from a linked file of Chemical Abstract Services (CAS) numbers.

The EPI Suite Interface screen (Fig. 5) has input lines where additional empirically derived physical data may be entered. Data available from the literature for the compounds of interest were entered into the program in a systematic way to determine their relative impact on the program output. Several model simulations were performed for each compound when empirical data were available. These included

- SMILES notation as the only input with the output file labeled No_Input;
- SMILES notation plus the melting point (MP) as input with the output file labeled _MP;

- SMILES notation plus the MP and water solubility (WS) as input with the output labeled `_WS`;
- SMILES notation plus the MP, WS, Henry's Law Constant (HLC) as input with the output labeled `_HLC`;
- SMILES notation plus the MP, WS, HLC, and vapor pressure (VP) as input with the output labeled `_VP`;
- SMILES notation plus the MP, WS, HLC, VP, and logarithm of the octanol–water partition coefficient (Log K_{ow}) as input with the output labeled `_Kow`.

EPI v3.11

File Edit Functions BatchMode ShowStructure Output Fugacity Other Help

PhysProp Previous Get User Save User CAS Input CALCULATE

Enter SMILES:

Enter NAME:

Henry LC (atm-m3/mole): Wat Sol (mg/L): MP:

Vap Pr (mm Hg): BP:

Water Depth (meters): River: Lake: Log Kow :

Wind Velocity (m/sec): Bio P (hr):


Current Velocity(m/sec): Bio A (hr):

Bio S (hr):

Output

☒ Summary

☐ Full



The EPI (Estimation Programs Interface) Suite™ was developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation (SRC). Important information on the application of the individual models contained within the EPI Suite™ is included in the EPI Suite™ User's Guide.

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Figure 5. EPI Suite input screen.

The model run output (full) were saved electronically and printed. The data then were transferred to spreadsheets for further evaluations, comparisons, and chart production.

Few empirically derived physical/chemical data are available for ADNA, ADNDNE, DNNC, and HCO. Nevertheless, using the chemical structures, EPI Suite estimated the chemical properties of the four chemicals. The estimated chemical properties from EPI Suite may provide adequate information for ranking the proposed chemicals in terms of their environmental mobility, persistence/bioaccumulation, and toxicity. However, it is also possible the estimates from EPI Suite may not adequately describe the ADNA, ADNDNE, DNNC, and HCO. Because there are very few direct measurements for these chemicals, it is not possible to “ground truth” the EPI Suite output for these chemicals. For example, ADNA and ADNDNE have not been synthesized.

In an effort to pseudo-ground-truth the EPI Suite model, an indirect method was employed evaluating four compounds analogous to the compounds of interest, but for which there are known chemical/physical properties. Analogue compounds were selected resembling the chemical structure of the four compounds of interest. Specifically, ammonium dinitramide (ADN) was selected as an analogue for ADNA; hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) was an analogue for DNNC; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was an analogue for HCO; and 1,1-diamino-2,2-dinitroethene (FOX-7) was an analogue for ADNDNE. The chemical structures shown in Figure 6 are included to permit visual comparisons of the compounds and their respective analogues.

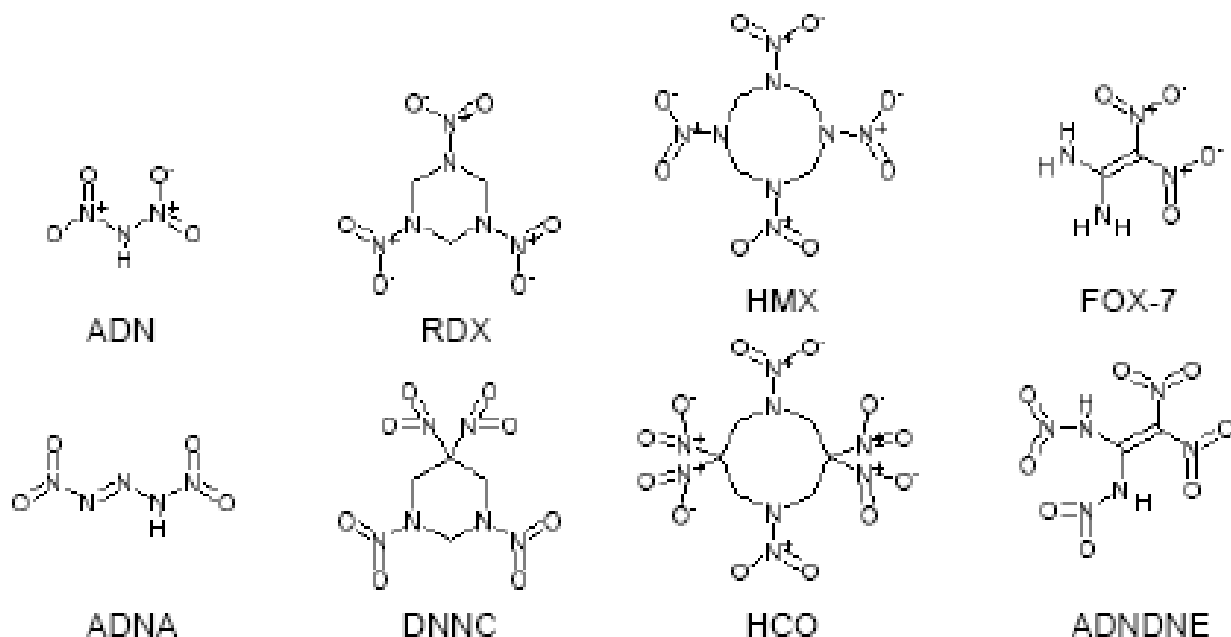


Figure 6. Compounds of interest and their analogues.

Initial examination of the compounds of interest using the EPI Suite software included adding a variety of physical and chemical input parameter values. The parameters selected to have additional value inputs were accessible on the top portion of the EPI Suite interface and included melting point, water solubility, Henry's Law Constant, vapor pressure, and the log K_{ow} . These data were entered into the interface when literature values were available. Other parameter value changes and methods of input remain to be examined to further refine and evaluate the proposed methodology.

Finally, in addition to the chemicals of interest and their analogs, AP was run through the EPI Suite software. The data for AP were used as a basis of comparison for the compounds of interest. The data for mobility, bioaccumulation, and toxicity for the compounds of interest were compared to those of AP.

The SMILES notations that follow (Table 1) were developed for the eight compounds and AP.

Table 1. Summary of SMILES notations for compounds of interest.

ADN	<chem>O=[N+](O)N[N+](O)=O</chem>
ADNA	<chem>O=[N+](O)N\N=N\N[N+](O)=O</chem>
RDX	<chem>O=[N+](O)N1CN([N+](O)=O)CN([N+](O)=O)C1</chem>
DNNC	<chem>O=[N+](O)C1([N+](O)=O)CN([N+](O)=O)CN([N+](O)=O)C1</chem>
HMX	<chem>O=[N+](O)N1CN([N+](O)=O)CN([N+](O)=O)CN([N+](O)=O)C1</chem>
HCO	<chem>O=[N+](O)C1([N+](O)=O)CN([N+](O)=O)CC([N+](O)=O)([N+](O)=O)CN([N+](O)=O)C1</chem>
FOX-7	<chem>N/C(N)=C([N+](O)=O)\N[N+](O)=O</chem>
ADNDNE	<chem>O=[N+](O)/C([N+](O)=O)=C(N[N+](O)=O)\N[N+](O)=O</chem>
AP	<chem>O=C(=O)(=O)ON(H)(H)(H)H</chem>

SMILES notation for each compound was input into EPI Suite utilizing the sequence described above. ADNA and ADNDNE have no empirical physical/chemical data in the literature because they have not been synthesized. Limited chemical/physical data were found—in some cases being limited to the melting point—for DNNC and HCO. ADNA and ADNDNE were run using the SMILES notation as the sole input. For the other compounds, EPI Suite was run iteratively with all other available literature-derived data as input. However, a systematic evaluation of the effect of EPI Suite inputs on model estimate outputs indicated melting point and K_{ow} were the parameters that, if included as model input, resulted in the greatest effect on model output when compared to the model output using SMILES notation as the sole input. As a result, the analysis presented herein reports and compares the EPI Suite model output when run using the following as model inputs:

1. SMILES notation alone;
2. SMILES notation and melting point; and
3. SMILES notation, melting point, and K_{ow} .

As mentioned above, the empirically derived melting point and/or K_{ow} were not available for all chemicals. As a result, in some cases the model input iterations were limited by the availability of data from the literature.

Where available, the EPI Suite output from these modeling runs is compared to its respective empirically based literature value(s). Also, the modeled data generated for the compounds of interest are contrasted with data generated for their respective analogs. Finally, the information known or estimated for AP is contrasted with the compounds of interest.

4 FINDINGS

Data summaries are presented from the EPI Suite model runs for both the compounds of interest and the analogue compounds. The following sections display summaries of the empirical data and EPI Suite results for each compound of interest. Following the display of data for the compound of interest, a similar display of data is provided for its analogue compound such as ADN for ADNA. Shading in the tables indicates where model output changed based on input. Evaluations of the EPI Suite outputs for compound of interest and analogue follow the data summaries.

4.1 ADNA and Its Analogue, ADN

Summaries of the modeling output for ADNA and ADN are included in this section². Table 2 summarizes the literature data and EPI Suite output for ADNA. Table 3 summarizes the literature and EPI Suite data for ADN.

EPI Suite-generated data for ADNA is based on the SMILES input alone (see Table 2). The results suggest ADNA is hydrophilic and highly water soluble (115,600 mg/L) and not likely to bioaccumulate. Lack of bioaccumulation is indicated by the relatively low estimated log K_{ow} (-0.14) and organic carbon partition coefficient ($K_{oc} = 3.36$), indicative of a compound not likely to partition into lipids. Log K_{ow} values are also directly proportional to aquatic toxicity, and values < 1 generally will not pose a problem to fish and wildlife. As such, ADNA is not likely to pose a hazard to aquatic biota or biomagnify in the food chain. However, the estimated value for K_{oc} also suggests ADNA will not sorb strongly to organic material in soils and other media.

² The EPI Suite model is unable to evaluate ionic bonds such as those found in ADNA. A surrogate for ADNA was used and can be viewed in Figure 5.

Table 2. Summary of ADNA literature values and EPI Suite input and output.

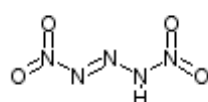
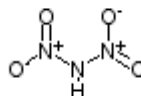
EPI Suite output	ADNA			
	Ammonium di(nitramido)amine			
Molecular formula	H ₁ N ₅ O ₄			
Molecular weight (g/mol)	135.04			
	Literature value	EPI Suite Input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state				
Melting point (°C)	NA ^a	273	Not run ^b	Not run ^b
Boiling point (°C)	NA	630	Not run ^b	Not run ^b
Solubility, water (mg/L)	NA	115,600	Not run ^b	Not run ^b
Partition coefficients				
Log K _{ow}	NA	-0.14	Not run ^b	Not run ^b
K _{oc} (L/kg)	NA	3.36	Not run ^b	Not run ^b
Vapor pressure (mm Hg at 25°C)	NA	2.3E-14	Not run ^b	Not run ^b
Henry's Law constant (atm-m ³ /mole)	NA	7.4E-09	Not run ^b	Not run ^b
Half-life in air (hours)	NA	100,000	Not run ^b	Not run ^b
Half-life in water (hours)	NA	360	Not run ^b	Not run ^b
Half-life in soil (hours)	NA	360	Not run ^b	Not run ^b
Half-life in sediment (hours)	NA	1,440	Not run ^b	Not run ^b
Daphnid LC50 (mg/L)	NA	9,502	Not run ^b	Not run ^b
LOEC (Daphnid EC50) (mg/L)	NA	191	Not run ^b	Not run ^b
Chemical structure				
Notes: a NA = Not available in researched literature b These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K _{ow} . MP Melting point				

Table 3. Summary of ADN literature values and EPI Suite input and output.

EPI Suite output	ADN			
	Ammonium dinitramide			
Molecular formula	H ₄ N ₄ O ₄			
Molecular weight (g/mol)	124.06			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state	Solid			
Melting point (°C)	92 ^a	246	246	Not run ^b
Boiling point (°C)	NA	571	571	Not run ^b
Solubility, water (mg/L)	500,000 ^a	1.0E+06	1.0E+06	Not run ^b
Partition coefficients				
Log K _{ow}	NA	-1.29	-1.29	Not run ^b
K _{oc} (L/kg)	NA	10.53	10.53	Not run ^b
Vapor pressure (mm Hg at 25°C)	~0	1.7E-12	9.6E-11	Not run ^b
Henry's Law constant (atm·m ³ /mole)	NA	1.3E-07	1.3E-07	Not run ^b
Half-life in air (hr)	NA	100,000	100,000	Not run ^b
Half-life in water (hr)	370 years ^a	360	360	Not run ^b
Half-life in soil (hr)	NA	360	360	Not run ^b
Half-life in sediment (hr)	NA	1,440	1,440	Not run ^b
Daphnid LC50 (mg/L)	NA	83,827	83,827	Not run ^b
LOEC (Daphnid EC50) (mg/L)	NA	1,019	1,019	Not run ^b
Chemical structure				
Notes: a Mill and Spangord, 1997 b These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K _{ow} . MP Melting point				

The estimated vapor pressure and Henry's Law constant for ADN are very low, indicating volatilization is not a likely transport pathway. The estimated half-life for ADN in air (100,000 hours) is based on hydrolysis and does not consider photolysis. However, others have suggested that

ADN has a photolysis half-life on the order of minutes (Mill and Spanggord 1997). Given the chemical similar structures, ADNA will likely photodegrade quickly as well. The estimates of half-life in water and soil, 360 hours each, are indicative of a compound that will degrade relatively slowly in the environment. At the surface of the soil or in the top of the water column, ADNA will likely degrade more quickly via photolysis than suggested by the model results for these media. However, for groundwater, subsurface soil, and surface water deeper than 1 m, the rate of degradation is estimated by the half-life to be > 360 hours.

Table 3 summarizes the literature and EPI Suite output for the ADN analogue, ADN. The empirically derived melting point for ADN is 92°C (Mill and Spanggord 1997), and contrasts sharply with the melting point predicted with EPI Suite of 245°C. However, empirical and modeled values for water solubility and vapor pressure generally agree. Both the literature value (Mill and Spanggord 1997) and EPI Suite model output for water solubility, 500,000 and 1,000,000 mg/L, respectively, are indicative of a highly water soluble chemical. Similarly, literature and EPI Suite values for vapor pressure agree, suggesting ADN is not readily volatilized under environmental conditions. Literature half-life values for water (Mill and Spanggord 1997) are very different from those estimated from EPI Suite, 370 years versus 360 hours, respectively. The reason for this discrepancy between the empirical and modeled data is unclear, but Mill and Spanggord (1997) state ADN is hydrolytically stable in water at environmentally relevant pHs at 25°C.

Also, Mill and Spanggord (1997) state biotransformation of ADN in soil and water, under aerobic and anaerobic conditions, was not observed, although it did degrade when a glucose substrate was added. However, ADN has been demonstrated to photolyze very rapidly. Finally, ADN is also estimated to have relatively low log K_{ow} , indicating it is not highly lipophilic and not likely to bioaccumulate (Berty et al. 1995; Grater et al. 1996, 1998). Log K_{ow} values are also directly proportional to aquatic toxicity, and values < 1 will not generally pose a problem to fish and wildlife (Dean and Channel 1995). As such, ADNA is not likely to pose a hazard to aquatic biota.

Taken together, the predicted high water solubility, low predicted K_{oc} , the relatively long half-lives for ADNA in soil and water, and the suggested

evidence from ADN's recalcitrant nature in soil and water indicate that ADNA, if introduced to the environment, would be readily mobilized by water and percolate through the vadose zone to groundwater and/or surface water. To the extent that ADNA is on the soil surface or near the top of the surface water column, photodegradation may play an important role in natural attenuation. However, once below the ground surface, in groundwater, or otherwise in a location without adequate sunlight, little decomposition via abiotic pathways may occur.

4.2 DNNC and Its Analogue, RDX

Table 4 summarizes the empirical and EPI Suite output for DNNC. As shown in Table 4, literature values for the melting point for DNNC were available and ranged from 151 to 154°C (Oyumi and Brill 1985a). EPI Suite estimates the melting point for DNNC to be 148°C using only the SMILES format as model input. For DNNC, the empirical and modeled melting points are in good agreement as opposed to ADN.

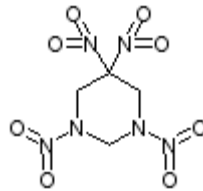
EPI Suite model output for DNNC water solubility ranges from 73,140 mg/L when using the SMILES notation alone to 50,100 mg/L when using both the SMILES notation and the literature value for melting point. Although there is a difference in predicted water solubility for the two EPI Suite model runs, the differences are relatively small, and both indicate DNNC is a relatively highly water soluble compound. However, of the four compounds of interest evaluated, DNNC is predicted to be the least soluble.

The predicted log K_{ow} for DNNC, -1.14, indicates this compound is not lipophilic and will not readily bioaccumulate and biomagnify in the food chain. Because low K_{ow} values are also indicative of low aquatic toxicity, this compound is not expected to pose a hazard to freshwater fish or macroinvertebrates. The predicted K_{oc} for DNNC is higher than predicted for ADNA, suggesting it may have a lower propensity for movement in soil and may sorb to soil and sediment more readily than ADNA. The predicted K_{oc} for DNNC is 1,678 L/kg, which is similar to some semi-volatile compounds, such as naphthalene, 933 L/kg (Price et al. 2001).

Like ADNA, DNNC is not likely to volatilize to the atmosphere once released to the environment. This is suggested from the very low predicted vapor pressures and Henry's Law constant. Nevertheless, EPI Suite pre-

dicts a rapid half-life, three hours, for DNNC released to the air, so its residence time and transport in the atmosphere may be limited.

Table 4. Summary of DNNC literature values and EPI Suite input and output.

EPI Suite output	DNNC or TNDA			
	1,3,5,5-Tetranitrohexahydropyrimidine			
Molecular formula	C ₄ H ₆ N ₆ O ₈			
Molecular weight (g/mol)	266.13			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES MP, and K _{ow}
Physical state				
Melting point (°C)	151–154 ^a	148	148	Not run ^b
Boiling point (°C)	NA	398	398	Not run ^b
Solubility, water (mg/L)	NA	73,140	50,100	Not run ^b
Partition coefficients				
Log K _{ow}	NA	–1.14	–1.14	Not run ^b
K _{oc} (L/kg)	NA	1,678	1,678	Not run ^b
Vapor pressure (mm Hg at 25°C)	NA	5.3E-07	4.8E-07	Not run ^b
Henry’s Law constant (atm·m ³ /mole)	NA	8.4E-15	8.4E-15	Not run ^b
Half-life in air (hours)	NA	3	3	Not run ^b
Half-life in water (hours)	NA	900	900	Not run ^b
Half-life in soil (hours)	NA	900	900	Not run ^b
Half-life in sediment (hours)	NA	3,600	3,600	Not run ^b
Daphnid LC50 (mg/L)	NA	152,000	152,000	Not run ^b
LOEC (Daphnid EC50) (mg/L)	NA	1,976	1,976	Not run ^b
Chemical structure				
Notes: a Oyumi and Brill 1985a b These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K _{ow} . MP Melting point				

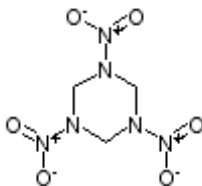
The predicted half-lives for DNNC in the other environmental compartments—water, soil and sediment—are double of those predicted for ADNA and ADN but similar to RDX.

Table 5 summarizes literature-derived and EPI Suite values for RDX. In this case, EPI Suite under-predicted the melting point of RDX by 60 percent—205°C (Oyumi and Brill 1985a) versus 133°C. In contrast, EPI Suite over-predicted the water solubility of RDX, 60 mg/L (Oyumi and Brill 1985a) by as much as two orders of magnitude when the EPI Suite input was limited to the SMILES notation (6,062 mg/L), and by a single order of magnitude (612 to 710 mg/L) when the melting point and/or K_{ow} inputs are provided. The contrast between the relatively low water solubility for RDX from the literature and predicted values of 50,100 to 73,140 mg/L for DNNC may be explained by the increased number of oxygens present on DNNC. The increased oxygen content of the molecule may allow for additional hydrogen bonding, which could result in higher water solubility. However, it is also possible the EPI Suites model is over-predicting the DNNC water solubility in the same way that it is over-predicting RDX water solubility.

The literature and predicted $\log K_{ow}$ for RDX agree, 0.94 (Oyumi and Brill 1985a) versus 0.68, respectively. However, a two-order-of-magnitude difference is seen between the literature (1.86 L/kg, Oyumi and Brill 1985a) and predicted K_{oc} (195 L/kg) for RDX. The difference may suggest the predicted K_{oc} for DNNC is overestimated. If this is the case, DNNC may be more mobile in soil, groundwater, and sediment than one might deduce from the EPI Suites predicted K_{oc} by itself.

The vapor pressures and Henry's law constant for RDX predicted by EPI Suite are several orders of magnitude greater than those found in the literature (Table 5). However, from an environmental fate and transport perspective, RDX would not be considered a volatile chemical regardless of whether literature or predicted values were used. Both values suggest RDX exposed to the air or dissolved in water would not readily volatilize into the atmosphere.

Table 5. Summary of RDX literature values and EPI Suite input and output.

EPI Suite output	RDX			
	Hexahydro-1,3,5-trinitro-1,3,5-triazine			
Molecular Formula	C ₃ H ₆ N ₆ O ₆			
Molecular Weight (g/mol)	222.12			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES MP, and K _{ow}
Physical state	Crystalline solid			
Melting point (°C)	204 - 206 ^a	133	133	133
Boiling point (°C)	NA ^b	353	353	353
Solubility, water (mg/L)	60 ^a	6,062	710	612
Partition coefficients				
Log K _{ow}	0.94 ^a	0.68	0.68	0.68
K _{oc} (L/kg)	1.86 ^a	195	195	195
Vapor pressure (mm Hg at 25°C)	2.0E-09 ^a	1.3E-06	1.4E-06	1.4E-06
Henry's Law constant (atm-m ³ /mole)	2.0E-11 ^a	6.3E-08	6.3E-08	6.3E-08
Half-life in air (hours)	10.7 – 168 ^c	1.043	1.043	1.043
Half-life in water (hours)	75 – 2.2E08 ^d	900	900	900
Half-life in soil (hours)	323 – 6E07 ^e	900	900	900
Half-life in sediment (hours)	NA	3,600	3,600	3,600
Daphnid LC50 (mg/L)	NA	2,804	2,804	1,636
LOEC (Daphnid EC50) (mg/L)	NA	81	81	53
Chemical structure				
Notes: a Meyer, 1977 b NA = Not available in researched literature c Sikka et al. 1980, Spanggord et al.1980a, b d Price et al. 1998, Spanggord et al. 1980a, b e Pennington et al. 2001, Deliman and Gerald 1998 MP Melting point				

Predicted half-lives in the four environmental compartments are nearly identical for RDX and DNNC, suggesting their persistence in the environment may be similar. RDX's presence has been documented in the groundwater at a number of manufacturing and military installations, suggesting DNNC may be similarly mobile.

4.3 HCO and Its Analogue, HMX

Table 6 summarizes the literature values and EPI Suite output for HCO. Like DNNC, an empirically derived melting point value of 250°C for HCO was available from the literature (Oyumi and Brill 1985a). Using the SMILES notation alone, EPI Suite computed a melting point of 221°C, which is in good agreement with the empirically derived value.

EPI Suite model output for HCO water solubility ranges from 384,100 mg/L when using the SMILES notation alone to 153,000 mg/L when using both the SMILES notation and the literature value for melting point. Although there is a difference in predicted water solubility for the two EPI Suite model runs, the difference is only a factor of 2.5. Nevertheless, both values for predicted water solubility indicate HCO is a relatively highly water-soluble chemical.

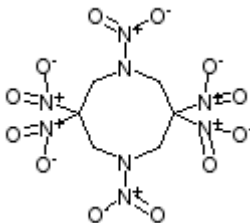
The predicted log K_{ow} for HCO, -2.28, indicates this compound is not lipophilic and thus will not readily bioaccumulate and/or biomagnify in the food chain. The low log K_{ow} is indicative of a low potential hazard to freshwater fish and wildlife. The predicted K_{oc} for HCO, 136,700, is the highest predicted for all of the compounds of interest. The high K_{oc} value indicates this compound will not move through soil and may sorb to soil and sediment more readily than the other compounds of interest. The predicted K_{oc} for HCO is similar to relatively persistent compounds such as polyaromatic hydrocarbons.

Given the predicted vapor pressure and Henry's law constant, HCO is not likely to volatilize to the atmosphere once released to the environment. The atmospheric residence time of HCO is likely to be small, given the predicted half-life of 48 hours.

The predicted half-lives in the other environmental compartments—water, soil, and sediment—are similar in magnitude to those predicted for the other compounds of interest. These results suggest introduction of HCO

into the environment as a dissolved species will result in a persistent and highly mobile compound, characteristics similar to HMX.

Table 6. Summary of HCO literature values and EPI Suite input and output.

EPI Suite output	HCO or HNDZ			
	1,3,3,5,7,7-Hexanitro-1,5-diazacyclooctane			
Molecular formula	C ₆ H ₈ N ₈ O ₁₂			
Molecular weight (g/mol)	384.18			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state				
Melting point (°C)	250 ^a	221	221	Not run ^b
Boiling point (°C)	NA ^a	525	525	Not run ^b
Solubility, water (mg/L)	NA	384,100	153,000	Not run ^b
Partition coefficients				
Log K _{ow}	NA	-2.8	-2.8	Not run ^b
K _{oc} (L/kg)	NA	136,700	137,000	Not run ^b
Vapor pressure (mm Hg at 25°C)	NA	5.1E-11	2.3E-11	Not run ^b
Henry's Law constant (atm-m ³ /mole)	NA	1.5E-23	1.5E-23	Not run ^b
Half-life in air (hours)	NA	48	48	Not run ^b
Half-life in water (hours)	NA	1,440	1440	Not run ^b
Half-life in soil (hours)	NA	1,440	1440	Not run ^b
Half-life in sediment (hours)	NA	5,760	5760	Not run ^b
Daphnid LC50 (mg/L)	NA	7.1E6	7.1E6	Not run ^b
LOEC (Daphnid EC50) (mg/L)	NA	44,700	44,723	Not run ^b
Chemical structure				

Notes:

a Oyumi and Brill 1985a

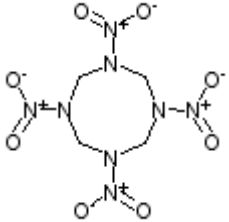
b These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K_{ow}.

MP Melting point

Table 7 summarizes the literature-derived and EPI Suite values for HMX. In this case, EPI Suite under-predicted the melting point of HMX by approximately 65 percent. In contrast, EPI Suite over-predicted the water solubility of HMX by as much as 2.5 orders of magnitude when the EPI Suite input was limited to the SMILES notation, and as much as two orders of magnitude when the melting point and K_{ow} were input into the model. Similar to the comparison made above for DNNC and RDX, the contrast between the relatively low water solubility for HMX from the literature, 5 to 6.63 mg/L, and that predicted for HCO, 153,000 to 384,100 mg/L, may be explained by the increased number of oxygens present on HCO. The increased oxygen content of the molecule may allow for additional hydrogen bonding, which could result in higher water solubility. However, it is also possible the EPI Suites model is over-predicting the HCO water solubility in the same way that it is over-predicting for HMX.

The literature and predicted $\log K_{ow}$ for HMX are in good agreement. However, a nearly 3.5 order-of-magnitude difference is seen between the literature and predicted K_{oc} for HMX (Table 7). The difference between the literature and predicted K_{oc} for HMX may suggest the predicted K_{oc} for HCO is overestimated. If this is the case, HCO may be more mobile in soil, groundwater, and sediment than one might deduce from just the EPI Suites predicted K_{oc} .

Table 7. Summary of HMX literature values and EPI Suite input and output.

EPI Suite output	HMX			
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine			
Molecular Formula	C ₄ H ₈ N ₈ O ₈			
Molecular Weight (g/mol)	296.16			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state	Crystalline solid			
Melting point (°C)	276–280 ^a	183	183	183
Boiling point (°C)	NA ^b	436	436	436
Solubility, water (mg/L)	5–6.63 ^a	2,556	131	579
Partition coefficients				
Log K _{ow}	0.06–0.26 ^a	0.82	0.82	0.82
K _{oc} (L/kg)	0.54 ^a	1,850	1,850	1,850
Vapor pressure (mm Hg at 25°C)	3.3E-14 ^a	2.4E-08	1.7E-09	1.7E-09
Henry’s Law constant (atm·m ³ /mole)	2.6E-15 ^a	8.7E-10	8.7E-10	8.7E-10
Half-life in air (hours)	4.6–168 ^c	0.78	0.78	0.78
Half-life in water (hours)	11–425 ^d	900	900	900
Half-life in soil (hours)	3.4E5 to 2.8E7 ^e	900	900	900
Half-life in sediment (hours)	NA	3,600	3,600	3,600
Daphnid LC50 (mg/L)	NA	2,788	2,788	1,135
LOEC (Daphnid EC50) (mg/L)	NA	85	85	259
Chemical structure				
Notes: a USACHPPM 2001 b NA = Not available in researched literature c Bedford et al. 1996, Spangford et al. 1983 d McCormick et al. 1984, Deliman and Gerald 1998 e Phelan and Webb 1998, Deliman and Gerald 1998 MP Melting point				

4.4 ADNDNE and Its Analogue, FOX-7

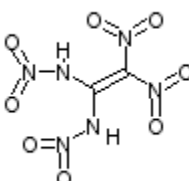
Table 8 summarizes the EPI Suite predictions for ADNDNE. No empirically derived data were found for ADNDNE in the reviewed literature. Based on the SMILES notation and EPI Suite output, ADNDNE appears to be a highly water-soluble chemical (232,800 mg/L). It also appears, from the very low predicted vapor pressures and Henry's Law constants, that once in the environment, ADNDNE will not readily volatilize. Also, the predicted K_{oc} , 928 L/kg, indicates ADNDNE will be moderately adsorbed by soil and sediment. Bioaccumulation and biomagnification of ADNDNE is not predicted to be significant, given the relatively low $\log K_{ow}$ of -1.54 . The potential to induce adverse effects to aquatic organisms is also low because the $\log K_{ow}$ value is less than one.

Similar to the other chemicals, ADNDNE is anticipated to quickly reduce by photolysis. Environmental degradation rates are less certain for water, soil, and sediment, but are similar to rates predicted for the other compounds of interest.

Table 9 summarizes the literature and EPI Suite predictions for FOX-7. The only literature value found for FOX-7 was the melting point. Table 9 shows that the EPI Suite-predicted melting point is less than half that reported in the literature using the SMILES notation alone. The effect on the EPI Suite output when using the literature value for the FOX-7 melting point is most notable for the estimated vapor pressure. When the literature value for melting point is used as input, the vapor pressure drops by 1.5 orders of magnitude. No other changes in EPI Suite output are noted.

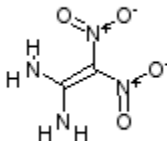
Given the paucity of empirical data for both the ADNDNE and its analogue, FOX-7, there is little certainty in the EPI Suite output for these compounds.

Table 8. Summary of ADNDNE literature values and EPI Suite input and output.

EPI Suite output	ADNDNE			
	Diammonium di(nitramido)dinitroethylene			
Molecular formula	C ₂ H ₂ N ₆ O ₈			
Molecular weight (g/mol)	238.07			
	Literature value	EPI Suite Input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state				
Melting point (°C)	NA ^a	127.89	Not run ^b	Not run ^b
Boiling point (°C)	NA	388.92	Not run ^b	Not run ^b
Solubility, water (mg/L)	NA	232,800	Not run ^b	Not run ^b
Partition coefficients				
Log K _{ow}	NA	-1.54	Not run ^b	Not run ^b
K _{oc} (L/kg)	NA	928	Not run ^b	Not run ^b
Vapor pressure (mm Hg at 25°C)	NA	1.5E-06	Not run ^b	Not run ^b
Henry's Law constant (atm-m ³ /mole)	NA	5.3E-14	Not run ^b	Not run ^b
Half-life in air (hours)	NA	138	Not run ^b	Not run ^b
Half-life in water (hours)	NA	900	Not run ^b	Not run ^b
Half-life in soil (hours)	NA	900	Not run ^b	Not run ^b
Half-life in sediment (hours)	NA	3,600	Not run ^b	Not run ^b
Daphnid LC50 (mg/L)	NA	315,000	Not run ^b	Not run ^b
LOEC (Daphnid EC50) (mg/L)	NA	3,430	Not run ^b	Not run ^b
Chemical structure				

Notes:
a NA = Not available in researched literature
b These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K_{ow}.
MP Melting point

Table 9. Summary of FOX-7 literature values and EPI Suite input and output.

EPI Suite output	FOX-7			
	1,1-Diamino-2,2-dinitroethene			
Molecular formula	C ₂ H ₄ N ₄ O ₄			
Molecular weight (g/mol)	148.08			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state				
Melting point (°C)	205-270 ^a	83	83	Not run ^b
Boiling point (°C)	NA	288	288	Not run ^b
Solubility, water (mg/L)	NA	1.0E+06	1.0E+06	Not run ^b
Partion coefficients				
Log K _{ow}	NA	-2.86	-2.86	Not run ^b
K _{oc} (L/kg)	NA	30.6	30.6	Not run ^b
Vapor pressure (mm Hg at 25°C)	NA	1.0E-3	4.7E-05	Not run ^b
Henry's Law constant (atm-m ³ /mole)	NA	1.4E-12	1.43E-12	Not run ^b
Half-life in air (hours)	NA	5.85	5.85	Not run ^b
Half-life in water (hours)	NA	360	360	Not run ^b
Half-life in soil (hours)	NA	360	360	Not run ^b
Half-life in sediment (hours)	NA	1,440	1,440	Not run ^b
Daphnid LC50 (mg/L)	NA	2,073	2,073	Not run ^b
LOEC (Daphnid EC50) (mg/L)	NA	—	—	Not run ^b
Chemical structure				

Notes:
a deKlerk et al. 2003, Karlsson et al. 2002
b These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K_{ow}.
MP Melting point

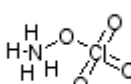
4.5 Ammonium Perchlorate

Ammonium perchlorate (AP) is evaluated here as a benchmark against which to gauge the other chemicals, since AP is the primary oxidizer in missiles and rockets and is being considered for replacement due to its environmental impact concerns. Table 10 summarizes the literature values and EPI Suite output for AP.

AP is a highly water-soluble chemical, with an empirically derived water solubility of 200,000 mg/L. EPI Suite predicts AP to be completely miscible in water (1,000,000 mg/L). The high solubility of AP is consistent with the fact that AP will dissociate, forming a readily water-soluble perchlorate anion. Table 10 also shows the predicted $\log K_{ow}$ is relatively low, indicating AP will not likely bioaccumulate or biomagnify within the food web. However, perchlorate has been measured in lettuce leaves and cows' milk, indicating that biotransfer does occur in the environment. The low $\log K_{ow}$ (< 1) is also a good predictor of a low potential to induce toxic effects on freshwater organisms. Also, the predicted K_{oc} for AP is indicative of its inability to sorb to soil and sediments.

As with the other compounds evaluated here, AP is not predicted to readily volatilize in the environment, based on the modeled vapor pressure and Henry's Law Constant. However, once in the environment, degradation is predicted to be moderate to slow, as suggested by the half lives in soil, sediment, and water.

Table 10. Summary of AP literature values and EPI Suite input and output.

EPI Suite output	AP			
	Ammonium perchlorate			
Molecular formula	NH ₄ ClO ₄			
Molecular weight (g/mol)	117.49			
	Literature value	EPI Suite input		
		SMILES only	SMILES and MP	SMILES, MP, and K _{ow}
Physical state				
Melting point (°C)	269			Not run ^a
Boiling point (°C)	NA	616	616	Not run ^a
Solubility, water (mg/L)	200,000	1.0E+06	1.0E+06	Not run ^a
Partition coefficients				
Log K _{ow}	NA	-5.84	-5.84	Not run ^a
K _{oc} (L/kg)	NA	96.6	96.6	Not run ^a
Vapor pressure (mm Hg at 25°C)	NA	2.8E-11	1.3E-13	Not run ^a
Henry's Law constant (atm-m ³ /mole)	NA	4.3E-18 ^b	2.1E-20 ^b	Not run ^a
Half-life in air (hours)	NA	100,000	100,000	Not run ^a
Half-life in water (hours)	NA	360	360	Not run ^a
Half-life in soil (hours)	NA	360	360	Not run ^a
Half-life in sediment (hours)	NA	1,440	1,440	Not run ^a
Daphnid LC50 (mg/L)	NA	1.3E+09	1.3E+09	Not run ^a
LOEC (Daphnid EC50) (mg/L)	NA	2.1E+06	2.1E+06	Not run ^a
Chemical structure				
Notes: MP Melting point a These iterations were not run in EPI Suite because empirical literature data were not found for melting point and/or K _{ow} . b VP/WS not a bond estimate.				

5 DISCUSSION OF RESULTS

The intent of this report is to assess the potential validity of the model predictions and to compare the fate-and-transport potential of the compounds of interest to that of AP. A summary of measured and model-estimated physical and chemical properties for the chemicals is provided in Appendix A. Also, a cursory evaluation of the toxicity of these compounds is presented below.

5.1 EPI Suite Model Validity

Although EPI Suite is capable of producing estimates of a variety of environmentally significant physical/chemical parameters, it does have limitations. For example, Zakikhani et al. (2002) state QSAR models such as EPI Suite can produce estimates of octanol–water partition coefficients with a mean error equivalent to the experimental mean error. However, Zakikhani et al. (2002) also state improved methods are still required for estimating biodegradation rates.

In this analysis, differences, especially between modeled and measured data, are most notable for water solubility and K_{oc} . This was the case for RDX and HMX, and in both cases, EPI Suite tended to overestimate the water solubility and the K_{oc} (Table 11). Given the similarities in the structures, it is possible the water solubility and K_{oc} predicted for their analogues, DNNC and HCO, also yield over-predictions.

Literature-derived and EPI Suite-generated vapor pressures differed by several orders of magnitude in some cases. However, because both literature value and estimated values were so low, the overall conclusion regarding the unimportance of the volatilization/air pathway is not affected.

Differences in empirically derived and modeled melting points were noted for ADN and FOX-7. However, other parameters, such as water solubility and vapor pressure, did not appear significantly affected by the differing melting point estimates.

Table 11. Comparison of measured and model predicted results.

	Melting Point (°C)	Water Solubility (ppm)	Log K _{ow}	K _{oc}	T _{1/2} Water (hr)	T _{1/2} Soil (hr)	Daphnid (ppm)
ADNA	273	1.2 X 10 ⁵	-0.14	3.4	360	360	9.5 X 10 ³
ADN	245 (92)	1.0 X 10 ⁶ (5 X 10 ⁵)	-1.29	10.53	360 (370 yr)	360	8.4 X 10 ⁴
DNNC	148 (151)	7.3 X 10 ⁴	-1.14	1678	900	900	1.5 x 10 ⁵
RDX	133 (204)	6.1 X 10 ³ (59.9)	0.68 (0.94)	195 (1.86)	900 (7.5-2.2 X 10 ⁸)	900 (6 X 10 ⁷)	2.8 X 10 ³
HCO	221 (250)	3.8 X 10 ⁵	-2.8	1.4 X 10 ⁵	1440	1440	7.1 X 10 ⁶
HMX	182 (276)	2.6 X 10 ³ (5)	0.82 (0.06)	1850 (0.54)	900 (11-425)	900 (2.7 X 10 ⁷)	2.8 X 10 ³
ADNDNE	127	2.3 X 10 ⁵	-1.54	928	900	900	3.2 X 10 ⁵
FOX-7	83 (205)	1.0 X 10 ⁶	-2.86	30.6	360	360	2.1 X 10 ³
AP	266 (240)	1.0 X 10 ⁶	-5.841	96.6	360	360	1.27 X 10 ⁹

Except for estimates of K_{oc} for HMX and RDX, the EPI Suite modeled data compared relatively well with the literature values when viewed from the standpoint of determining relative fate and transport. For example, even though the literature and EPI Suite predicted water solubility for HMX and RDX to be significantly different, the overall conclusions reached by this assessment (i.e., these chemicals are much less soluble than the other chemicals evaluated) still remain true. Viewing the output data in this way enables interpretation and use of the EPI Suite data even when the absolute accuracy of the EPI Suite output is unknown.

5.2 Fate and Transport Comparison

The EPI Suite model predictions of high solubility and low vapor pressure indicate the majority of the chemicals of interest introduced to the environment as residues on soil would end up in groundwater (Table 11). This would be especially true for the ionic compounds that would, in all likelihood, readily dissolve in water. The solubility estimates for HCO and DNNC might be overestimated, given they are saturated ring structures and their analogue compounds demonstrated significant differences between empirical and model estimated solubility. The predicted solubility of DNNC is approximately one-quarter the water solubility of AP. However,

as mentioned above, the predicted DNNC water solubility (Table 11) may be an overestimate, so the differences with AP may be even greater.

Lack of substituted halogens such as chlorine and $K_{ow} (< 1)$ suggest these compounds would not bioconcentrate, bioaccumulate, or biomagnify in fish and/or wildlife. This is true for the compounds of interest as well as for AP. The low K_{ow} values may not preclude biotransfer from the environment to biota, but will likely diminish the potential for lipophilic biomagnification.

Similarly, the aquatic toxicity QSAR estimates from EPI Suite indicate that, at anticipated environmental concentrations in the low ug/L range, these compounds would not directly pose a hazard to freshwater fish or macroinvertebrates (Table 12). Based on the toxicity values predicted by EPI Suite for the *Daphnia* species (i.e., LD₅₀ and Lowest Observed Effect Concentrations [LOEC]), all of the toxic endpoints would be expected to fall in the milligram-per-liter range. Indeed, the lowest LD₅₀ and LOEC predicted for *Daphnia spp.* was, respectively, 2,788 and 191 mg/L. This is well outside of any concentration that might be anticipated in ground-water. However, at manufacturing facilities, it is possible to find part-per-million levels of these compounds in surface water; for example, AP has been found in surface waters near manufacturing facilities well in excess of thousands ppm (Dottie and Roberson 2005).

Table 12. EPI Suite predicted environmental results.

Replacement	Water Mobility	Soil Migration	Degradation @ Surface	Degradation @ Subsurface	Bioaccumulation	Aquatic Toxicity
ADNAN	High	High	High	Med-Low	Low	Low
DNNC	High	Med-Low	High	Med-Low	Low	Low
HCO	High	Low	High	Med-Low	Low	Low
ADNDNE	High	Med	High	Med-Low	Low	Low
AP	High	High	Low	Low	Low	Low

The half-lives in water estimated by the EPI Suite model are relatively long. The oxygen uptake rate for a mixed culture of microorganisms could provide information regarding biodegradation or inhibition. Another way to test biodegradability is by conducting bench-scale tests utilizing wastewater (e.g., biological oxygen demand tests). Nevertheless, the half-life estimates in soil, sediment, and water for the compounds of interest are not significantly different from those for AP, indicating that, if released into the environment, they have the potential to be highly mobile.

Although photolysis may play an important part in the removal of these munitions residues from soils, hard surfaces, or the top shallow layer of surface waters, EPI Suite does not have methods for estimating half-lives for this degradation pathway. As a result, there is a high level of uncertainty in the air half-life estimates. Even if photolysis is found to be a significant degradation pathway for these chemicals, the half-lives in groundwater and subsurface soil may still remain relatively long.

5.3 Toxicological Comparison

From the standpoint of predicting or anticipating inherent toxicity, RDX would be a good working “surrogate” for DNNC; similarly, HMX would be a good surrogate for HCO, and ADN would be a fair surrogate for ADNA. Although very few toxicity data could be found, it appears that reproductive and/or carcinogenic endpoints may drive future *in vitro* or *in vivo* hazard assessments, as seen with the ADN studies (Berty et al. 1985; Kincaid et al. 1994, 1995; Steel-Goodwin et al. 1995a, 1995b). Most of these compounds, once absorbed into the body, would be anticipated to be reduced in the liver (nitrate reduction to the amino- or diamino-compound) and excreted as either the mono- or diamino-substituted derivative or further transformed to more soluble metabolites via Phase I or II enzyme systems. Because of the expected metabolic recognition via the high substitution with nitrate groups, these compounds also would not be expected (based on professional judgment) to have a very long half-life in the body, and thus the possibility of a highly idiosyncratic toxic mechanism, such as AP, also would be unlikely.

6 CONCLUSIONS AND RECOMMENDATIONS

Taken altogether, the four compounds assessed using the EPI Suite program are predicted to have physicochemical parameters that, once released into the general environment, may favor migration to surface water or groundwater. The low lipophilic nature of these compounds, as estimated by very low predicted log K_{ow} coefficients, also suggests these compounds would not bioconcentrate into aquatic organisms, nor would they bioaccumulate or biomagnify within the food chain. Direct toxicity to aquatic organisms, as estimated by QSAR-derived aquatic toxicity endpoints, is also expected to be very low.

Preliminary calculations based on the reproductive toxicology of ADN indicate acceptable drinking water (or groundwater if potable) concentrations that range between 340 and 1,015 $\mu\text{g/L}$ (depending on the use and/or conservatism of uncertainty factors).

Compared to AP, the compounds of interest are anticipated to behave similarly from an environmental fate-and-transport perspective. However, it is possible that HCO and DNNC are much less soluble in water than AP. Also, it is anticipated all of the compounds of interest will readily photodegrade. However, rates of degradation in subsurface soil, groundwater, deep surface water, and sediment appear highly variable and may be dependent on covariables not evaluated for this assessment.

This assessment also suggests there is some uncertainty in several of the EPI Suite Model outputs (e.g., melting point, water solubility, K_{oc}). Given that there are no empirical data to compare modeled data against for many of the compounds of interest, the uncertainty about these factors remains unquantified. It is recommended additional analyses examining the impact of changing the parameter values that remained fixed in the initial assessment, as well as evaluating the individual programs and their respective outputs when the programs are not utilized as a subroutine for the EPI Suite program, be undertaken. This recommendation includes conducting additional literature database searches for physical/chemical parameters for the compounds of interest. Specifically, additional investigation and translation of the Russian literature is recommended. Also, a

thorough evaluation of the contents of the Chemical Propulsion Information Agency at Johns Hopkins University is recommended. Finally, this recommendation includes conducting additional modeling on other surrogate compounds, such as 2,2-dinitropropane or 2-azo-2-nitropropane.

If, based on additional literature searches, the database of empirically derived information for the compounds of interest remains scant, it is further recommended that laboratory testing be considered for the determination of the most important parameters affecting fate and transport in the environment (water solubility, K_{ow} , etc.). This suggestion is made with the understanding that analytical methods may not be available for these chemicals. As such, analytical method development may be a necessary counterpart to this recommendation. In any case, as these compounds continue to move through the various military evaluations and closer to small-scale production, it will be important to supplement this screening level assessment of fate and transport in the environment with additional data.

Finally, it is recommended that a protocol be developed that systematically describes the steps that should be followed when evaluating new energetic chemicals from an environmental liability standpoint. The protocol should start with a screening level evaluation as described here, but should also clearly identify additional steps for evaluation. The additional steps, which will likely be more resource-intensive than a screening level assessment, should provide more detailed information about the chemicals of interest and their behavior in the environment. Also, the protocol should progress in a manner that removes uncertainty often found in screening level assessments and generate more conclusive information about a chemical's fate and toxicity.

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Appendix A: Estimated and Measured Chemical Parameters for Explosive Compounds

Compound	Initialism	MW (g)	Density (g/cm ³)	MP (°C)	K _{ow} (L/kg)	K _{oc} (L/kg)	K _d (L/kg)	Water solubility (mg/L)	Henry's Law Constant (atm-m ³ /mol)	Solid VP (mm Hg)	Diffusion coef (air) (cm ² /sec)	Diffusion coef (water) (cm ² /sec)	Soil T _{1/2} (days)	Water T _{1/2} (days)	Photolysis (hours)	Hydrolysis (years)
Ammonium di (nitramido) amine	ADNA	135.04	NA	273	0.72	3.36	NA	115,600	7.45E-09	2.30E-14	NA	NA	15	15	NA	NA
Ammonium dinitramide	ADN	124.06	NA	92 [C]	0.05	10.53	NA	500,000	1.27E-07	1.71E-12	NA	NA	15	135,050	NA	NA
1,3,5,5,-Tetra-nitrohexahydro-pyrimidine	DNNC	266.13	1.83 [A]	151–154 [D,E,F]	0.072	1,678	NA	50,100–73,140	8.39E-15	5.27E-07	NA	NA	37.5	37.5	NA	NA
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	222.26	NA	204–205 [A,G]	0.86 [G,J]	0.8–4.2 [J,K,L,M,N]	0.2–7.8 [A,J,P,R,S,T]	40–75.7A [G,J,L,W,X,Y,Z]	6.58E-12–2E-05 [A,B,G,J,N]	1.0–4.1E-09 [A,J,N,X]	0.074 [B]	7.15E-06 [B]	0.17–13,140 [G,AA,AB,AC,AD]	3–9E+06 [N,AB,AC,AD,AE]	13–168 [L,M,O]	1.7 [AH]
1,3,5,7-Hexanitro-1,5-diazacyclooctane	HCO	384.18	1.90 [B]	250	0.002	136,700	NA	153,000–348,100	1.53E-21	5.08E-11	NA	NA	240	60	NA	NA
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	296.16	NA	276–286 [B,G]	0.06–0.13 [G]	2.8–6.3 [B,J,OP]	< 1–13.3 [R,V]	2.6–6.6 [G,J,Y]	2.60E-15 [B,J]	3.3E-13–5.7 [B,J,O]	0.063 [B]	6.02E-06 [B]	1.4E+04 – 1.17E+06 [G,AA,AB]	0.5–18 [O,AB,AG]	4.6–168 [O,AG]	NA
Diammonium di (nitramido) dinitroethylene	ADNDNE	238.07	NA	128	0.029	928	NA	232,800	5.27E-14	1.45E-06	NA	NA	37.5	37.5	NA	NA
1,1-Diamino-2,2-dinitroethene	FOX-7	148.08	NA	205–270 [H,I]	0.0014	31	NA	1.00E+06	1.43E-12	1.04E-03	NA	NA	15.8	15.8	NA	NA
Perchlorate		99.5	NA	610	NA	NA	0.83 [V]	2.50E+05	1.40E-06	NA	NA	NA	NA	NA	NA	NA

Note: Bolded and italicized entries are predicted values based on EPI Suite simulations.

Appendix A, cont'd

Coef	Coefficient	M	Spanggord et al. 1990a
Hg	Mercury	N	Spanggord et al. 1990b
K _d	Soil partitioning coefficient	O	Spanggord et al. 1983
K _{oc}	Organic carbon partitioning coefficient	P	Talmage et al. 1999
K _{ow}	Octanol water partitioning coefficient	Q	Hale et al. 1979
MP	Melting point	R	Leggett 1985
MW	Molecular weight	S	Selim and Iskandar 1994
NA	Not available	T	Speitel et al. 2002
T _{1/2}	Half-life	U	Townsend and Myers 1996
VP	Vapor pressure	V	Susarla et al. 1999
A	Ainsworth et al. 1993	W	Fleming et al. 1996
B	Rosenblatt et al. 1989	X	Phelan and Webb 1997
C	Brill et al. 1963	Y	Gorontzy et al. 1994
D	Hendrickson and Shackelford 2004	Z	Hawari et al. 2000
E	Oyumi and Brill 1985	AA	Phelan and Webb 1998
F	Mill and Spanggord 1997	AB	Deliman and Gerald 1998
G	Tomkins 2000	AC	Price et al. 1998
H	deKlerk et al. 2003	AD	Pennington et al. 2001
I	Karlsson et al. 2002	AE	Cataldo et al. 1990
J	Groom et al. 2002	AF	McCormick et al. 1984
K	Rosenblatt 1986	AG	Bedford et al. 1996
L	Sikka et al. 1990	AH	Hoffsommer et al. 1972

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14. ABSTRACT A screening level assessment of the fate, transport, and toxicity of four potential replacements for perchlorate was performed. Resulting data will allow for evaluation and minimization of the potential environmental liability associated with the use of energetic compounds as propellants. This report details methods used and assessment findings. Inorganic oxidizer ammonium di(nitramido)amine (ADNA); cyclic nitramine/gem-dinitro compound 1,3,5,5-tetranitrohexahydropyrimidine (DNNC); 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HCO); and diammonium di(nitramido)dinitroethylene (ADNDNE) were evaluated. Their respective analogue compounds also were evaluated: ammonium dinitramide (ADN); hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); and 1,1-diamino-2,2-dinitroethene (FOX-7). Evaluations of ammonium perchlorate (AP) provide a point of comparison. From an environmental fate and transport perspective, it appears ADNA, ADNDNE, DNNC, and HCO may have some characteristics similar to AP. However, it is possible HCO and DNNC are much less soluble in water than AP, thereby reducing the likelihood of environmental transport. It also is anticipated that ADNA, ADNDNE, DNNC, and HCO will readily photodegrade. However, rates of degradation in subsurface soil, groundwater, deep surface water, and sediment appear highly variable and may be dependent on covariables not evaluated for this assessment. Because of uncertainty with the model predicted results, recommendations for additional analysis, which could yield compound-specific data and reduce uncertainty, are provided.					
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